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(54) Cleaning, disinfecting and bleaching composition

(57) The invention relates to a composition suitable for cleaning, disinfection and bleaching comprising an acidic aqueous solution of hydrogen peroxide, a surfactant, a phosphonic acid based complexing agent and citric acid. The invention also relates to use of such a composition for disinfection, bleaching, removal of stains from textiles, or removal of lime deposits.

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Description

The present invention relates to an acidic aqueous composition suitable for cleaning, disinfection and/or bleaching comprising hydrogen peroxide, as well as use of such a composition.

Hard surface cleaning and disinfection, laundry bleaching and stain-removal, domestic as well as industrial, is often performed with chlorine based chemicals such as hypochlorite in aqueous solution which generally is effective for disinfection and bleaching, or organic solvents, enzymes and surfactants effective for stain-removal. However, hypochlorite is not useful for removing lime soap and it may also damage textile fibres and the original colours thereof. Further, for environmental reasons it is desirable to avoid chlorine based cleaning agents.

Hydrogen peroxide is known as an environmental friendly oxidiser and disinfectant, but to be efficient a rather high concentration and/or a long contact time is necessary. In the bacterial cell hydrogen peroxide reacts with -SH groups and thereby destroys SH containing enzymes and inhibit the protein synthesis. However, hydrogen peroxide has a poor storage stability, particularly in combination with other ingredients such as surfactants or organic acid. Although the hydrogen peroxide stability can be improved by addition of chelating agents like phosphonates, it is hard to find a phosphonate that both is biodegradable and effective as a hydrogen peroxide stabiliser.

EP-B1-87049 discloses a composition for disinfection comprising hydrogen peroxide, an acidic phosphorous compound such as phosphoric acid, and a complexing agent selected from certain phosphonic acids or salts thereof.

EP-A1-517996 discloses a hydrogen peroxide based bleaching composition comprising a specific class of surfactants.

WPI Acc. No 93-004727/01, abstract of JP-A-4332800 discloses a detergent composition comprising hydrogen peroxide, an organic or inorganic acid, and a carboxylic acid type polymer.

WPI Acc. No 88-004846/01, abstract of JP-A-62270509 discloses a composition for removing marine creatures from constructions used in sea water, the composition comprising citric acid, hydrogen peroxide and a surfactant.

WO 93/14183 discloses a detergent composition comprising a surfactant, oxygen bleach such as hydrogen peroxide and a metal sequestering agent.

WO 91/08981 discloses a solution for stabilizing hydrogen peroxide comprising citric acid, tartaric acid and phosphoric acid.

WO 94/07803 discloses the use of a composition comprising an oxidising agent, an organic acid and a phosphonic acid for removing magnetite deposits in water supply systems.

It is an object of the present invention to provide a

storage stable composition based on hydrogen peroxide which is effective for several functions including cleaning, bleaching, disinfection, removal of stains on textiles and removal of lime deposits. It is another object of the invention to provide a composition only containing environmentally acceptable components. The composition according to the invention comprises an acidic aqueous solution of hydrogen peroxide, a surfactant, citric acid and a complexing agent based on phosphonic acid, dipicolinic acid or derivatives thereof. Suitably, the pH of the composition is below 4 preferably below 3, most preferably below 2, which improves the antimicrobial activity as well as the capability of removing lime deposits or lime soap in, for example, bath tubs, toilet bowls or the like. A low pH also improves the stability of the hydrogen peroxide. However, the pH preferably is above about 0.5, most preferably above about 1.

It has surprisingly been found that citric acid, unlike most environmental friendly acids, does not cause any substantial decomposition of the hydrogen peroxide in aqueous compositions also containing surfactants and phosphonic acid or dipicolinic acid based complexing agents. It is preferred that, apart from citric acid and phosphonic and/or dipicolinic acids or derivatives thereof, the composition does not contain any substantial amounts of other organic acids. From an environmental point of view it is also preferred that the composition does not comprise any substantial amounts of phosphoric acid or phosphates.

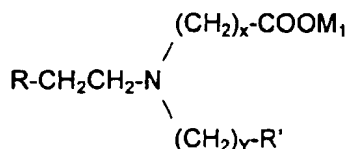
The surfactant facilitates removal of dirt and especially non-ionic surfactants are excellent on removing fat and pigments but they also enhance the antimicrobial effect as they destroy bacterial cell membranes. Preferred surfactants are compatible with hydrogen peroxide in acidic solutions which means that neither do they cause decomposition of the hydrogen peroxide, nor does the hydrogen peroxide or the acid cause decomposition of the surfactants. Further, the surfactants are preferably environmental friendly and biodegradable.

The composition contains one or several different surfactants. Preferably, it comprises a non-ionic surfactant or an amphoteric surfactant or a mixture thereof. Although not preferred, it is also possible to include anionic surfactants as an alternative or as a complement.

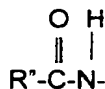
Preferred non-ionic surfactants are selected from ethoxylated fatty acids, alcohols, amines or amides, preferably comprising from 1 to 12 most preferably from 4 to 8 mols ethylene oxide per mol acid, alcohol, amine or amide. Preferably the acid, alcohol or amide comprises from 7 to 15, most preferably from 9 to 11 carbon atoms. Useful non-ionic surfactants can be high foaming such as an ethoxylated alcohol containing 11 carbon atoms and 8 ethylene oxides, or low foaming such as a narrow range ethoxylated alcohol containing 9 carbon atoms and 6 ethylene oxides.

Preferred amphoteric surfactants are selected from derivatives of preferably aliphatic amines comprising one or more anionic groups such as carboxy, sulfo, or

sulfato. Particularly preferred amphoteric surfactants satisfy the formula:



wherein x and y are, independently from each other, from 1 to 5, R' is -COOM₂ or -OH, M₁ and M₂ are, independently from each other, H, ammonium or an alkali metal such as Na, K or Li, R is a straight or a branched carbon chain having from 1 to 8 carbon atoms or an amide of the formula:

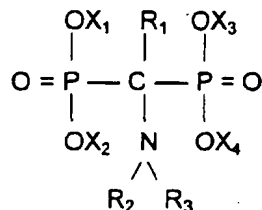


wherein R'' is a straight or a branched carbon chain having from 1 to 8 carbon atoms. It is preferred that R' is COOM₂ and that R is a straight or a branched carbon chain. Examples of preferred amphoteric surfactants are octylimino dipropionate and capryloampho diacetate which are commercially available under the trademarks Ampholak® YJH40 (Akzo Nobel) and Ampholak® XJO (Akzo Nobel), respectively.

At least one complexing agent based on phosphonic acid, dipicolinic acid or derivatives thereof should be included in order to obtain satisfactory storage stability of the hydrogen peroxide. One or several phosphonic acid based complexing agents is preferably present in an amount from about 0.5 wt% to about 10 wt%, most preferably from about 1 wt% to about 4 wt% based on the content of hydrogen peroxide. Dipicolinic acid or derivatives thereof may be present in an amount from about 0.25 to about 5 wt%, preferably from about 0.5 to about 2 wt% based on the content of hydrogen peroxide. The complexing agents also enhance the microbial effect since they chelate cat-ions like magnesium and calcium which have an important role in the bacterial cell. Examples of useful derivatives of dipicolinic acid are picolinic acid, acid, 2,6-pyridine dialdehyde or 2,2-dipyridyl amine. Examples of useful phosphonic acid based complexing agents are those that are commercially available such as 1-hydroxyethylidene-1,1-diphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, aminotri (methylenephosphonic acid), ethylene diamine tetra (methylenephosphonic acid), hexamethylene diamine tetra (methylenephosphonic acid), diethylenetriamine penta (methylenephosphonic acid) and diethylenetriamine hexa (methylenephosphonic acid), as well as salts thereof. Particularly high stability can be achieved by including both a phosphonic acid and dipi-

colinic acid or a derivative thereof.

Preferred phosphonic acid based complexing agents are those that are at least partly biodegradable. Therefore, the composition preferably comprises a complexing agent selected from biodegradable 1-aminoalkane-1,1-diphosphonic acids, or salts thereof, preferably of the formula:



wherein R₁ is selected from hydrogen, C₁-C₄ alkyl and phenyl; R₂ and R₃, independently from each other, are selected from hydrogen, C₁-C₂₂ alkyl, C₅-C₆ cycloalkyl, phenyl, C₇-C₁₈ alkylphenyl, C₇-C₁₈ phenylalkyl, a C₁-C₁₀ alkanol radical, a carboxy alkyl radical having up to 10 carbon atoms, wherein R₂ and R₃ together with the nitrogen atom can form a piperidino, pyrrolidino or a morpholino group; and X₁ to X₄, independently from each other, are selected from hydrogen, alkali metal and ammonium. Preparation of such phosphonic acids are described in, for example, US 3899496, US 3979385 and "Synthesis of 1-dialkylaminoalkylidene diphosphonic acids and their properties for complex formation", Fukuda, M., et al, Yukagaku, Vol. 25, No. 6, pp. 362-64 (1976).

Preferably R₁ is hydrogen. It is also preferred that R₂ and R₃ are selected from hydrogen, C₁ to C₄ alkyl, or together with the nitrogen form a morpholino group. Particularly preferred complexing agent are selected from morpholinomethane diphosphonic acid, N,N-dimethyl aminodimethyl diphosphonic acid, aminomethyl diphosphonic acid, or salts thereof, preferably sodium salts.

A composition of the invention can be in the form of a concentrate intended to be diluted before use. Such a concentrate may suitably contain from about 10 wt% to about 60 wt%, preferably from about 30 wt% to about 50 wt% of hydrogen peroxide, from about 5 wt% to about 30 wt%, preferably from about 10 wt% to about 20 wt% of surfactants, from about 0.5 wt% to about 10 wt% preferably from about 1 wt% to about 5 wt% of citric acid, and from about 0.05 wt% to about 10 wt%, preferably from about 1 wt% to about 5 wt% of phosphonic acid based complexing agents, alternatively from about 0.025 to about 5 wt%, preferably from about 0.5 to about 2.5 wt% of dipicolinic acid or derivatives thereof. The balance is preferably mainly made up of water. The pH of the concentrate is suitably from about 0.5 to about 3, preferably from about 1 to about 2. Such a composition is preferably diluted from about 10 to about 50 times before use and is then particularly suitable for cleaning

and disinfection of hard surfaces, particularly in the food industry where it is important to destroy human pathogenic as well as product spoiling micro-organisms and spores.

A ready to use composition suitable for cleaning, disinfection or stain removal in households suitably contains from about 0.1 wt% to about 10 wt%, preferably from about 4 wt% to about 6 wt% of hydrogen peroxide, from about 0.1 wt% to about 10 wt%, preferably from about 2 wt% to about 6 wt% of surfactants, from about 0.1 wt% to about 3 wt% preferably from about 0.5 wt% to about 1 wt% of citric acid, and from about 0.01 wt% to about 5 wt%, preferably from about 0.1 wt% to about 1 wt% of phosphonic acid based complexing agents, alternatively from about 0.005 to about 2.5 wt%, preferably from about 0.05 to about 0.5 wt% of dipicolinic acid or derivatives thereof. The balance is preferably mainly made up of water. The pH of the composition is suitably from about 1 to about 4, preferably from about 2 to about 3. The composition is very effective for cleaning hard surfaces in kitchens and bathrooms and for removing stains from textiles. It can also be used outdoors for removing or inhibiting growth of mould or algae on wood or other materials. If appropriate, it can be combined with other cleaning agents or detergents, such as ordinary alkaline detergents for machine washing.

A composition of the invention can easily be prepared by simply mixing the components to desired concentrations.

The invention also relates to use of a composition as described herein for disinfection, bleaching, removal of stains from textiles, or removal of lime deposits.

The invention is further illustrated through the following examples which, however, are not intended to limit the scope of the invention. If not otherwise stated, all contents and percentages refer to % by weight.

Example 1: A composition according to the invention consisting of an aqueous solution of 5% of hydrogen peroxide, 5% of ethoxylated C₁₀-C₁₄ fatty alcohols with 7 mols ethylene oxide and 1 mol propylene oxide as a high foaming non-ionic surfactant, 0.2% of morpholinomethane diphosphonic acid disodium salt and 1% of citric acid was prepared by mixing the components. The pH was 2.3. The stability of the hydrogen peroxide was tested by storing the composition 42 days at 40°C. It was found that 95.9% of the hydrogen peroxide remained.

Example 2: A composition according to the invention consisting of an aqueous solution of 5% of hydrogen peroxide, 2.5% of ethoxylated C₁₀-C₁₄ fatty alcohols with 7 mols ethylene oxide and 1 mol propylene oxide as a high foaming non-ionic surfactant, 2.5% of ethoxylated C₁₆-C₁₈ amide with 4 mols ethylene oxide as a low foaming non-ionic surfactant, 0.2% of morpholinomethane diphosphonic acid disodium salt and 1% of citric acid was prepared by mixing the components. The pH was 2.5.

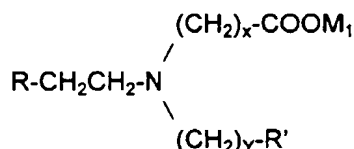
The stability of hydrogen peroxide was tested by storing the composition 42 days at 40°C. It was found that 96.6% of the hydrogen peroxide remained.

Example 3: A composition A according to the invention consisting of an aqueous solution of 4.9% of hydrogen peroxide, 50 g/l of ethoxylated C₁₀-C₁₄ fatty alcohols with 7 mols ethylene oxide and 1 mol propylene oxide as a high foaming non-ionic surfactant, 2 g/l of morpholinomethane diphosphonic acid disodium salt and 10 g/l of citric acid was prepared by mixing the components. The pH was 2.3. A composition B according to the invention was prepared in the same way with the exception that 1-hydroxyethylidene-1,1-diphosphonic acid was used instead of morpholinomethane diphosphonic acid which gave a pH of 1.8. The stability of the hydrogen peroxide was tested by storing the compositions 830 days at room temperature (about 20-25°C). It was found that the hydrogen peroxide concentration after storage was 3.9% in composition A and 2.9% in composition B.

Claims

1. Composition suitable for cleaning, disinfection and/or bleaching **characterised** in that it comprises, an acidic aqueous solution of hydrogen peroxide, a surfactant, citric acid, and a complexing agent based on phosphonic acid, dipicolinic acid or derivatives thereof.
2. Composition as claimed in claim 1, **characterised** in that the pH of the aqueous solution is below 4.
3. Composition as claimed in claim 2, **characterised** in that the pH of the aqueous solution is below 3.
4. Composition as claimed in any one of the claims 1-3, **characterised** in that the composition does not comprise any substantial amounts of phosphoric acid or phosphates.
5. Composition as claimed in any one of the claims 1-4, **characterised** in that the composition comprises a phosphonic acid based complexing agent.
6. Composition as claimed in any one of the claims 1-5, **characterised** in that the composition comprises a complexing agent based on dipicolinic acid or derivatives thereof.
7. Composition as claimed in any one of the claims 1-6, **characterised** in that the composition comprises as a complexing agent any of picolinic acid, dipicolinic acid, 2,6-pyridine dialdehyde or 2,2-dipyridyl amine.

8. Composition as claimed in any one of the claims 1-7, **characterised** in that the composition comprises a non-ionic surfactant or an amphoteric surfactant or a mixture thereof which is compatible with hydrogen peroxide in acidic solution.
9. Composition as claimed in claim 8, **characterised** in that the composition comprises an amphoteric surfactant satisfying the formula:

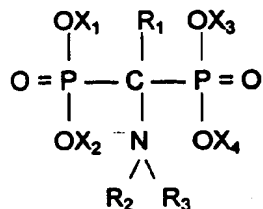


wherein x and y are, independently from each other, from 1 to 5, R' is -COOM₂ or -OH, M₁ and M₂ are, independently from each other, hydrogen, ammonium or an alkali metal, R is a straight or a branched carbon chain having from 1 to 8 carbon atoms or an amide of the formula:



wherein R'' is a straight or a branched carbon chain having from 1 to 8 carbon atoms.

10. Composition as claimed in claim 9, **characterised** in that R' is COOM₂.
11. Composition as claimed in any one of the claims 9-10, **characterised** in that R is a straight or a branched carbon chain.
12. Composition as claimed in any one of the claims 1-11, **characterised** in that the composition comprises a chelating agent selected from biodegradable 1-aminoalkane-1,1-diphosphonic acids, or salts thereof, of the formula:



wherein R₁ is selected from hydrogen, C₁-C₄ alkyl

and phenyl; R₂ and R₃, independently from each other, are selected from hydrogen, C₁-C₂₂ alkyl, C₅-C₆ cycloalkyl, phenyl, C₇-C₁₈ alkylphenyl, C₇-C₁₈ phenylalkyl, a C₁-C₁₀ alkanol radical, a carboxy alkyl radical having up to 10 carbon atoms, wherein R₁ and R₂ together with the nitrogen atom can form a piperidino, pyrrolidino or a morpholino group; and X₁ to X₄, independently from each other, are selected from hydrogen, alkali metal and ammonium.

13. Composition as claimed in claim 12, **characterised** in that the composition comprises a chelating agent selected from morpholinomethane diphosphonic acid, N,N-dimethyl aminodimethyl diphosphonic acid, aminomethyl diphosphonic acid, or salts thereof.
14. Use of a composition according to any of the claims 1-13 for disinfection, bleaching, removal of stains from textiles, or removal of lime deposits.

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EUROPEAN SEARCH REPORT

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EP 97 20 3428

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 634 476 A (PROCTER & GAMBLE) 18 January 1995 * examples 1-6 * * claims 1-13 * ---	1-4,6-8,14	C11D3/39 C11D3/36 C11D3/20 C11D3/28 //C11D1/66, C11D1/88
E	EP 0 829 533 A (PROCTER & GAMBLE) 18 March 1998 * page 11, Formulation III * ---	1-5,8,14	
D,X	WO 94 07803 A (HENKEL KGAA) 14 April 1994 * page 10, line 4 - line 11 * * claims 1-10 * ---	1-5,8,14	
X	EP 0 349 153 A (CLOROX CO) 3 January 1990 * page 6, line 25 - line 30 * * claims 1-4 * ---	1-4,8,14	
X	EP 0 432 776 A (KA0 CORP) 19 June 1991 * page 4, line 18 - line 21 * * claim 1 * ---	1-5,8,14	
A	US 4 880 566 A (BAEHR BERND D ET AL) 14 November 1989 * column 3, line 25 - line 37 * * claims 1-7 * ---	1,4,5,8,14	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
A	WO 95 12029 A (AKZO NOBEL NV ;BOELEMA ELTJO (NL); NAVARRO CHARLES MANUEL (NL); OL) 4 May 1995 * claims 1-3 * ---	1,14	
A	US 4 752 354 A (BEURICH HARALD ET AL) 21 June 1988 * claims 1-6 * ---	1,12,14	
		-/-	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 January 1999	Examiner Richards, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	<p>DATABASE WPI Section Ch, Week 9720 Derwent Publications Ltd., London, GB; Class D21, AN 97-224523 XP002087528 & RU 2 066 991 C (KARTAVCHENKO A V) , 27 September 1996 * abstract *</p> <p>---</p>	1	
A	<p>EP 0 141 355 A (BENCKISER KNAPSACK GMBH) 15 May 1985 * claims 1,2 *</p> <p>---</p>	1	
A	<p>US 4 534 945 A (HOPKINS QUENTIN G ET AL) 13 August 1985 * claim 1 *</p> <p>-----</p>	1	
The present search report has been drawn up for all claims			<p>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</p>
Place of search THE HAGUE		Date of completion of the search 11 January 1999	Examiner Richards, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>..... & : member of the same patent family, corresponding document</p>	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 97 20 3428

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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11-01-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0634476 A	18-01-1995	AU 7355394 A	13-02-1995
		JP 9500379 T	14-01-1997
		WO 9502667 A	26-01-1995
		US 5759989 A	02-06-1998
EP 0829533 A	18-03-1998	AU 4418397 A	02-04-1998
		WO 9811191 A	19-03-1998
WO 9407803 A	14-04-1994	DE 4232612 A	31-03-1994
		EP 0662931 A	19-07-1995
EP 0349153 A	03-01-1990	AU 2213292 A	29-10-1992
		AU 3710489 A	04-01-1990
		JP 2045600 A	15-02-1990
		US 5180514 A	19-01-1993
EP 0432776 A	19-06-1991	JP 2602563 B	23-04-1997
		JP 3188198 A	16-08-1991
		US RE35000 E	25-07-1995
		US 5118436 A	02-06-1992
US 4880566 A	14-11-1989	DE 3545909 A	25-06-1987
		BR 8606416 A	13-10-1987
		EP 0233350 A	26-08-1987
		IN 167841 A	29-12-1990
		JP 2063752 C	24-06-1996
		JP 7096680 B	18-10-1995
		JP 62164800 A	21-07-1987
		US 4959075 A	25-09-1990
WO 9512029 A	04-05-1995	AT 165636 T	15-05-1998
		AU 678631 B	05-06-1997
		AU 7992794 A	22-05-1995
		BR 9407905 A	26-11-1996
		CA 2175062 A	04-05-1995
		CN 1133622 A	16-10-1996
		CZ 9601212 A	11-12-1996
		DE 69409967 D	04-06-1998
		DE 69409967 T	05-11-1998
		EP 0725854 A	14-08-1996
		ES 2118445 T	16-09-1998
		FI 961774 A	25-04-1996
		NO 961661 A	25-04-1996
		NZ 274840 A	26-05-1997
		US 5641386 A	24-06-1997

EPO FORM P449

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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11-01-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4752354 A	21-06-1988	DE 3531563 A	05-03-1987
		CA 1332665 A	25-10-1994
		FI 861481 A,B,	05-03-1987
		JP 2533104 B	11-09-1996
		JP 63211393 A	02-09-1988
		SE 467162 B	01-06-1992
		SE 8603593 A	05-03-1987
EP 0141355 A	15-05-1985	DE 3338260 C	25-07-1985
		DE 3471705 A	07-07-1988
US 4534945 A	13-08-1985	CA 1224910 A	04-08-1987
		JP 1736509 C	26-02-1993
		JP 4024282 B	24-04-1992
		JP 60239305 A	28-11-1985